

PORPHYRIN DYAD SENSITIZERS FOR PHOTOELECTROCHEMICAL CELLS

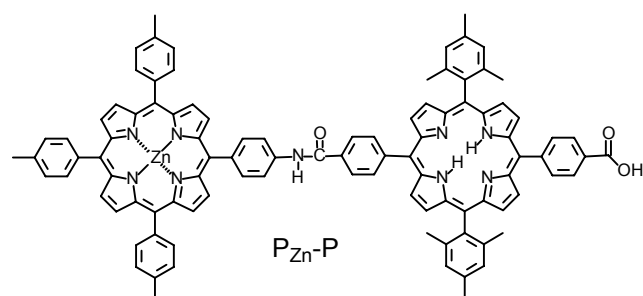
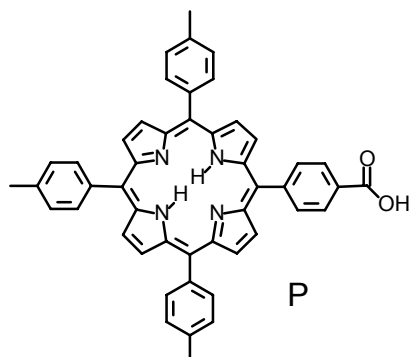
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A large variety of organic and inorganic dyes have been investigated as sensitizers in photoelectrochemical cells based on nanoparticulate metal oxide electrodes.^{1,2} There are potential advantages to using two or more covalently-linked dye moieties as sensitizers, rather than a single chromophore:

- A second chromophore can act as an antenna, transferring singlet excitation energy to the first and expanding the absorption cross section and spectral response of the cell.
- A second chromophore can inject electrons directly into the semiconductor, leading to photocurrent.
- Hole migration between the chromophores can slow charge recombination, increasing the quantum yield of useful current.

Two recent reports have suggested that under some conditions, porphyrin dyads may offer improvements over monomeric porphyrins as sensitizers.^{3,4} In order to further investigate this question, we have studied monomeric porphyrin **P** and dyad **P_{Zn}-P** as sensitizers.



Nanoparticulate tin (IV) oxide electrodes (nSnO₂) were prepared by spraying a dilute suspension of nSnO₂ onto clean sheets of conductive glass, consisting of an indium-doped tin (IV) oxide (ITO) layer on a glass support. After air drying, the particles were sintered by heating in air. The resulting electrodes were soaked in a solution of the porphyrin sensitizer to form a molecular monolayer on the nanoparticulate surface. These electrodes formed part of a photoelectrochemical cell with a platinum wire counter electrode. The electrolyte was a nitrogen-purged aqueous solution of sodium acetate (0.1 M) that contained hydroquinone (QH₂) as the redox relay. Short-circuit photocurrents were measured as the difference in currents observed between the ITO/nSnO₂

and platinum wire electrodes with and without incident light.

Figure 1 shows the absorption spectra of the porphyrin monomer and the dyad on the electrode surface.

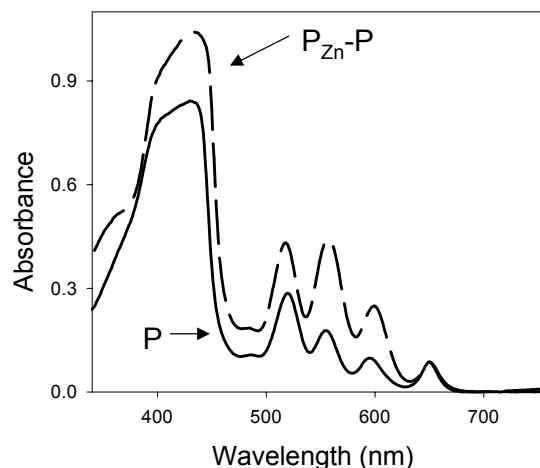


Figure 1

Figure 2 shows the results of a typical experiment, expressed as the incident photon to current efficiency (IPCE). It is clear from this example that both the

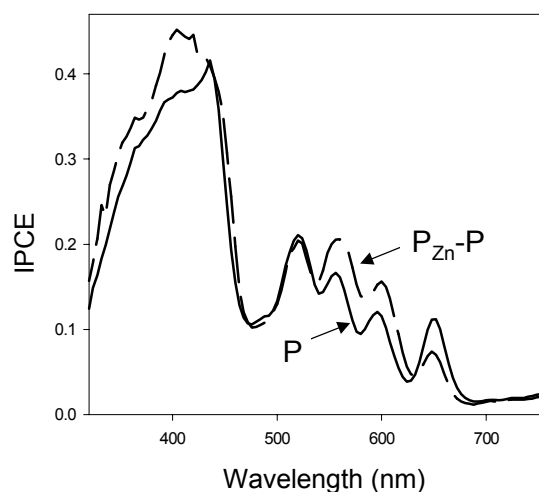


Figure 2

free base porphyrin (bound to the electrode via the carboxylic acid group) and the zinc porphyrin contribute to the photocurrent. This indicates singlet-singlet energy transfer between the chromophores and/or direct injection of an electron into the nanoparticulate semiconductor by the zinc porphyrin moiety. The relative IPCE and quantum yield of current originating from light absorbed by each porphyrin has been investigated as a function of variables such as light intensity and QH₂ concentration in order to extract more information concerning the details of electron injection, hole migration and energy transfer.

References

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